

Charge screening and magnetic anisotropy in RCo_5 compounds

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Abstract

An analysis of magnetic anisotropy in RCo_5 compounds is performed with account of screening of ion point charges by conduction electrons. A crucial role of non-uniform distribution of screening electrons (the terms containing derivatives of charge density) is demonstrated. Influence of anisotropy of screening, that is connected with the anisotropy of the Fermi surface, on the magnetic anisotropy sign is discussed.

It is believed now that the main mechanism of occurrence of strong magnetic anisotropy (MA) in the rare-earth (RE) based intermetallic systems is the crystal field one [1,2]. The simplest point-charge model leads frequently to difficulties and contradictions with experimental data. For example, the calculated MA constant K_1 in RCO_5 compounds turns out to be very large and have an incorrect sign [3]. Similar difficulties occur for the $\text{R}_2\text{Fe}_{14}\text{B}$ systems [4]. Thus screening of the crystal field should play an important role. This screening can be taken into account by introducing the effective ion charge Q^* which can differ considerably from the bare ion charge. Shielding of crystal fields in ionic solids [8] turns out to be insufficient even for qualitative explaining experimental data.

Another approach to the MA problem is based on the first-principle band-structure calculations. Generally, RE systems are a difficult case for standard band theory methods, so that one has to use some approximations and model representations (e.g., atomic sphere approximation in early papers, inclusion of f -states in the core states). Modern calculations [5,6] treat mainly the anisotropic contribution of the conduction electrons in the atomic sphere with the centre at the RE f -ion, and the rest “lattice” contribution is obtained in the point-charge approximation with screened charge densities of other cells, which do not overlap with the f -shell. It should be noted that the atomic and lattice contribution are in fact not independent, and their partial cancellation takes place. The local-spin-density full-potential approaches, which are based on total energy calculations [6], can provide correct orders of magnitude of anisotropy energy, but quantitative agreement with experimental data is not satisfactory.

Thus simple qualitative considerations which start from the physically transparent point-charge picture, but introduce effective distance-dependent ion charges, seem still be useful. In the present paper we analyze the first MA constant with account of charge screening by conduction electrons in a metal. As demonstrated in Ref. [7], effective charges depend strongly on the concrete form of screening electron density. In particular, the Friedel oscillations of charge density can play an important role. Here we discuss the screening in more details, in particular with account of its anisotropic character.

The MA constants are determined from angle dependence of the energy of magnetic ions in the crystal field

$$\delta\mathcal{E}_{cf} = -K_1 \cos^2 \theta + \dots \quad (1)$$

We consider the magnetic ion at the point $\mathbf{r} = 0$ in the crystal field of the surrounding charges. The contribution to the crystal-field potential from the ion with the bare charge Q_0 at the point \mathbf{R} can be represented as

$$V_{cf}(\mathbf{r}) = \frac{Q_0 + Q_{el}(\mathbf{R} - \mathbf{r})}{|\mathbf{R} - \mathbf{r}|} \quad (2)$$

where $Q_{el}(\mathbf{R})$ is the conduction-electron screening charge. After expanding (2) in r up to r^2 , the expression for K_1 can be written in the form (cf. Refs. [3,7])

$$K_1^{pc} = 3e^2 \Lambda \langle r_f^2 \rangle \alpha_J J(J - 1/2) \quad (3)$$

Here $\langle r_f^2 \rangle$ is the average square of the f -shell radius, J is the total angular momentum of the RE ion, α_J is the Stevens factor,

$$\Lambda = \sum_{\mathbf{R}} Q^*(\mathbf{R}) \frac{3 \cos^2 \theta_{\mathbf{R}} - 1}{R^3}, \quad (4)$$

the sum goes over the lattice, $\theta_{\mathbf{R}}$ is the polar angle of the vector \mathbf{R} , $Q^*(\mathbf{R})$ are the corresponding screened ion charges. Note the difference of our consideration from Ref. [5], where the screening charge in the sphere with the centre at the magnetic RE ion was calculated.

In the spherical charge density approximation we have [7]

$$Q^*(\mathbf{R}) = Q_0 + Q_{el}(R) - \frac{4}{3} \pi R^3 [Z(R) - RZ'(R)] \quad (5)$$

where $Q_{el}(R)$ is the conduction electron charge inside the sphere with the centre at the point charge and radius R ,

$$Q_{el}(R) = 4\pi \int_0^R \rho^2 d\rho Z(\rho) \quad (6)$$

$Z(R)$ is the charge density, $Q'_{el}(R) = 4\pi r^2 Z(R)$, the system of units where the electron charge $e = -1$ being used. We see that $Q^*(\mathbf{R})$ includes explicitly, besides the total charge

$Q_{el}(R)$, also the charge density $Z(R)$ and its derivative $Z'(R)$. Such terms do not occur in the calculations [5] where the “lattice” charge density does not overlap with the f -shell. Note that higher-order anisotropy constants are obtained after keeping next-order terms in r and include higher-order derivatives of $Z(R)$.

To obtain the value of $Q^*(\mathbf{R})$, one has to investigate the charge screening for a concrete electronic spectrum. In Ref. [7], the one-centre screening problem was considered within a simple model of free conduction electrons ($E = k^2/2$) in the rectangular potential well which is induced by single impurity and has the width d and depth $E_0 = k_0^2/2$ [9]. This model enables one to calculate the charge distribution of screening conduction electrons in terms of the spherical Bessel and Neumann functions $j_l(kr)$ and $n_l(kr)$ ($r > d$) and the scattering phase shifts η_l . The value of k_0 is determined for given k_F and d from the Friedel sum rule

$$Q_0 = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \eta_l(k_F) \quad (7)$$

The parameter d should be determined by the geometry of the lattice near the impurity. In Ref. [9], where impurities in the Ag host were considered, d was chosen to be equal to the Wigner-Seitz radius, so that $k_F d = 2$. The results of the calculations for $k_F d = 2$ and $k_F d = 3$ are presented in Figs.1,2. At $Q_0 = 1$ Eq.(7) yields $k_0 d = 1.46$ and $k_0 d = 1.235$ respectively.

The model discussed is more adequate for impurities which induce strong disturbance of charge density (e.g., in hydrogen-containing RE systems [10]). Of course, the choice of d may be different and more complicated models are required for a regular lattice of screened charges where interference of screening charge clouds from different centres takes place. In metals, the value of ion charge Q_0 can be put to the charge in some sphere (e.g., charge transfers in the atomic sphere were considered in Ref. [5]) and does not necessarily coincide with the nominal free ion value. Besides that, the dependence $Q^*(\mathbf{R})$ in the lattice can become anisotropic. Nevertheless, we use Figs.1-2 for a qualitative discussion.

One can see from Fig.2 that at $R < d$, except for the case of very small R where $Q^*(R)$ slightly decreases, the derivative term in (5) results in that $Q^*(R)$ grows (despite an increase

of $|Q_{el}(R)|$). For $R \simeq d$, where Z' is maximum, the non-uniform distribution of electron density leads to that the effective ion charge Q^* is positive and exceeds considerably its bare value Q_0 ($Q_0 = 1$ in our case). At the same time, with further increasing R the situation changes drastically: Z' decreases and becomes negative, so that “overscreening” of the ion charge occurs. At large distances Q^* tends to zero, but considerable oscillations of the effective charge sign take place, which attenuate rather slowly. It should be stressed that the oscillations are due mainly to the derivative term. On the other hand, the quantity $Q_0 + Q_{el}(R)$ monotonically decreases up to $R \simeq d$ and then tends to zero very rapidly, oscillations being very weak (Fig.1). This agrees with the fact that band calculations yield usually small values of charge transfers in atomic spheres (see, e.g., [5]). The oscillation period and position of maxima and minima of $Q^*(R)$ turn out to be weakly sensitive to the values of Q_0 and d , but are determined mainly by the parameter k_F .

Now we analyze concrete geometry of the RCo_5 lattice (CaCu_5 structure, Fig.3) with $c \simeq 4\text{\AA}$, $a \simeq 5\text{\AA}$. The Co ions have two positions in two different types of hexagonal layers: $2c$ (CoI) sites in the layers containing R atoms with $R = a/\sqrt{3} \simeq 0.57a$ and $3g$ (CoII) sites in layers with no R atoms with $R = \frac{1}{2}\sqrt{a^2 + c^2} \simeq 0.64a$. Although positions of all R ions are equivalent, the contributions to the crystal field at a given R site from the charges in the same plane (sites RI, $R = a$) and in neighbor planes (sites RII, $R = c$) can be different, since the effective charge is a function of the distance between two sites. Then we can write down (cf. [3])

$$\Lambda = 6a^{-3} \left(16 \frac{2y^2 - 1}{(1 + y^2)^{5/2}} Q_{\text{CoII}}^* - 3^{3/2} Q_{\text{CoI}}^* + \frac{2}{3} y^{-3} Q_{\text{RII}}^* - Q_{\text{RI}}^* \right) \quad (8)$$

where $y = c/a \simeq 0.8$. The contributions of in-plane (I) and out-of-plane (II) neighbors of R site have different signs. However, unlike the pure rare earth-metals with the hcp structure [1], the small geometrical factor $\sqrt{8/3} - c/a = 1.633 - c/a \sim 0.05$ does not occur, so that the calculated value of K_1 turns out two orders of magnitude larger.

The experimental data on the c/a ration and first magnetic anisotropy constant of the RCo_{5+x} compounds at low temperatures are presented in Table 1. A monotonic decrease of

c/a in the RE series takes place (with exception of tetravalent Ce).

Table 1. The total angular momenta J , Stevens factors α_J , average squares of the f -shell radius $\langle r_f^2 \rangle$ (atomic units) for free R ions; c/a ratios and the experimental values of K_1 (K/RE ion) in RCo_{5+x} systems [for light R according to [11,12] and for heavy R (the contribution of RE sublattice) according to Ref. [13]]. The corresponding values of $\overline{Q}_{\text{Co}}^*$ are calculated by using (9), (3).

RCo_{5+x}	CeCo ₅	PrCo ₅	NdCo ₅	SmCo ₅	TbCo _{5.1}	DyCo _{5.2}	HoCo _{5.2}	ErCo ₆
J	5/2	4	9/2	5/2	6	15/2	8	15/2
$\alpha_J \times 100$	-5.7	-3.4	-7.1	4.1	-1.0	-0.63	-0.22	0.25
$\langle r_f^2 \rangle$	1.20	1.09	1.00	0.88	0.76	0.73	0.69	0.67
c/a	0.817	0.797	0.796	0.795	0.803	0.810	0.817	0.821
K_1^{exp}	-61	-44	-220	190	-96	-211	-203	80
$\overline{Q}_{\text{Co}}^*$	-0.007	-0.003	-0.006	-0.04	-0.02	-0.03	-0.09	-0.04

One can see that the experimental values K_1^{exp} for heavy rare earths and Sm are obtained for $\Lambda a^3 \simeq 1$. Taking into account only the contributions of Co ions in (8) and assuming $Q_{\text{CoI}}^* = Q_{\text{CoII}}^* = \overline{Q}_{\text{Co}}^*$ we obtain

$$\Lambda \simeq -\frac{23.4}{a^3} \overline{Q}_{\text{Co}}^* \quad (9)$$

Thus, for $\overline{Q}_{\text{Co}}^* \sim 1$, K_1 has incorrect sign and is very large in absolute value (of order of 3000K). It should be noted that such values of K_1 are in fact not self-consistent: they would destroy the Russel-Saunders coupling and quench total momenta. In light rare earths (Ce, Pr, Nd and Sm) the momenta, as obtained from both neutron scattering and magnetization measurements [14], are indeed considerably suppressed. Ce ions are supposed to be tetravalent; for other light rare earths, effects of the strong crystal fields and exchange interactions can play a role. On the other hand, in Tb, Dy, Ho and Er the saturation momenta are close to their free ion values [15].

To compensate large numerical factor in (9), one has to put $\overline{Q}_{\text{Co}}^*$ to be very small in absolute value and negative (Table 1). One cannot rule out that the distance between Co

ions corresponds to negative values of Q^* with $|Q^*| \ll 1$ in Fig.2, but such a situation is rather unusual. Thus the simple model with equal Co charges can hardly explain the observed sign and value of K_1 , and a more detailed treatment of screening is needed.

An assumption that main role in the crystal field formation belongs to R ions and Q_{Co}^* can be assumed zero was made in Refs. [16,12]. The effective charges for R ions, Q_{R}^* , could be supposed to equal about 1, as well as in pure rare earths where this parameter varies between 1.1 and 1.4 [7]. Then we would obtain the correct sign and order of magnitude for K_1 since the contribution of RII ions dominates. However, the distances between RE ions in RCo_5 , c and a , are considerably larger than in pure rare earths (about 3.5\AA), so that the values Q_{R}^* can be much smaller. Besides that, the variation of effective charge in the RCo_5 series is much stronger than for pure rare earths. Such a variation can be related to the contribution of CoII sites since the factor at the first term in the brackets of (8) depends appreciably on $y = c/a$.

It is instructive to take into account the anisotropy of screening of Co charges that is connected with the anisotropy of the Fermi surface in the hexagonal lattice. Then the screening is determined by the wavevector of the Fermi surface in the corresponding direction. The effective values of k_F in the hexagonal planes can be supposed smaller than in the direction to CoII sites. Then the charge of the CoII ions is screened with distance slower than for CoI ions and can dominate in K_1 , despite the larger distance and numerical factor in (8). This circumstance may lead also to additional (besides pure geometrical) strong dependence of the anisotropy on y . It should be noted that the calculation for SmCo_5 [5] yields for charge transfers in the Co atomic spheres (as well as for CoI and CoII magnetic moments) different values: $q_{\text{CoI}} \simeq 0$, $q_{\text{CoII}} \simeq -0.03$.

Experimental values of K_1 from Table 1 can be obtained, e.g., for $Q_{\text{CoII}}^* \simeq 4Q_{\text{CoI}}^* \simeq 0.3$, $Q_{\text{R}}^* = 0$, or for $Q_{\text{CoII}}^* \simeq 3Q_{\text{CoI}}^* \simeq 0.2$, $Q_{\text{R}}^* \simeq 1$ (in the latter case, the sign of K_1 is determined by R contribution which is partially cancelled by the Co contribution). Thus occurrence of very small values of Q_{Co}^* by accidental reasons is not required in such a consideration.

To conclude, an account of distance-dependent screening of ion charges by conduction

electrons can provide a reasonable explanation of the first MA constant value in RCo_5 compounds, the non-uniform distribution of screening electrons (the derivative term in the expression for the effective charge (5)) being of crucial importance. Our approach does not introduce artificial separation into atomic spheres. On the other hand, it has a number of other drawbacks. In particular, it treats independent charge centres and is not self-consistent: perturbation of charge density by R ion itself (see, e.g., Ref. [3]) is not taken into account. Thus a synthesis of our consideration with approaches, that are based on the real electronic structure calculations, would be of interest for further insight into the problem of magnetic anisotropy in the rare-earth systems.

FIGURE CAPTIONS

Fig.1. The distance dependence of the sum of the bare ion charge and electron screening charge, $Q_0 + Q_{el}(R)$, for $k_F d = 2$ (solid line) and $k_F d = 3$ (dashed line) with $Q_0 = 1$.

Fig.2. The distance dependence of the effective charge $Q^*(R)$ (5) for the same parameter values as in Fig.1.

Fig.3. The local environment of the R site in the crystal structure of RCo_5 compounds. Large open circles denote R sites, small open circles CoI (2c) sites, small shaded circles CoII (3g) sites.

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